The Electron Density Distribution in a Mimoun Type Molybdenum Oxoperoxo Complex: Software Development for Heavy Atom Multipolar Analysis and Implications for Olefin Epoxidation by Peroxo Transition Metal Complexes

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There is a large general interest in understanding the nature of the bonding between dioxygen species and transition metals. Synthetically great sophistication has been achieved in the development of new complexes and catalytic oxidation by transition metal peroxo complexes is an important industrial process. However, the reaction mechanisms for e.g. olefin epoxidation are still far from understood. To obtain information about the electronic ground state of a typical molybdenum oxoperoxo catalyst we have measured single crystal diffraction data at X3A1 on $MoO(O_2)$(HMPA)-(dipic) at 20 K using a CCD detector. Before carrying out a complete analysis of the data it was necessary to modify the multipole electron density program XD to include atoms with 5 filled shells (such as Mo). Thus, the least squares and the property calculation routines have been modified to allow use of 5s and 4d orbitals. Moreover, in the data bank new non-relativistic and relativistic wave functions have been included and tested. Subsequently we have modeled the synchrotron X-ray data and carried out a complete topological analysis of the experimental electron density. The electrostatic potential and the Laplacian function clearly show that the crucial peroxo function maintains a large negative charge also after coordination. This indicates that direct attack by the olefin on the peroxo function (the Sharpless mechanism) is unlikely. The experimental electron density has furthermore been compared with high-level *ab initio* theoretical calculations in order to mutually validate the description of the chemical bonding in the complex by the two methods.

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